

Fig. 2. The molecular packing (PLUTO, Motherwell & Clegg, 1978).

The disruption of the planarity leads to a higher toxicity of the molecule and overall a lower biological activity which confirms the fact that the antitumour properties of the molecule can be induced by its intercalation between two adjacent base pairs of DNA. The activity seems to be related to the planarity of the molecule which is in accordance with a postulated intercalative process.

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## Structure of 2,2,6,6-Tetramethylpiperidinium Bromide, $C_9H_{20}N^+.Br^-$

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**Abstract.**  $M_r = 222$ ,  $P2_12_12_1$ ,  $a = 8.885(2)$ ,  $b = 9.300(2)$ ,  $c = 13.089(2)$  Å,  $U = 1081.6$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.36$  g cm<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 37.1$  cm<sup>-1</sup>,  $F(000) = 464$ ,  $T = 293$  K,  $R = 0.040$  for 883 observed unique reflections. The piperidinium ring has a distorted chair conformation. Comparison of the structure with that of similar compounds is made.

**Introduction.** The 2,2,6,6-tetramethylpiperidyl (tmp) ligand has been used for the stabilization of main-group compounds with low coordination numbers (Lappert, Power, Slade, Hedberg, Hedberg & Schomaker, 1979; Nöth, Staudigl & Wagner, 1982). We were interested,

therefore, in the possibility of synthesizing the diphosphene, (tmp)P=P(tmp). We have found, however, that the reaction of (tmp)PBr<sub>2</sub> (Markovskii, Romanenko & Ruban, 1979) with Mg in tetrahydrofuran results in the dimer, [(tmp)P]<sub>4</sub>, and traces of 2,2,6,6-tetramethylpiperidinium bromide. Presumably the latter product arose *via* hydrolysis of either (tmp)PBr<sub>2</sub> or [(tmp)P]<sub>4</sub>.

The X-ray crystal structure of the bromide salt does, however, provide interesting structural information, particularly when compared with the more widely studied 4-substituted tetramethylpiperidyl compounds (Cygler, Markowicz, Skolimowski & Skowroński, 1980).

**Experimental.** (2,2,6,6-Tetramethylpiperidino)phosphorus dibromide was prepared by literature procedure (Markovskii, Romanenko & Ruban, 1979); treatment of this product with Mg in refluxing tetrahydrofuran for 5 h resulted in tetrakis(2,2,6,6-tetramethylpiperidino)cyclotetraphosphane as the primary product on the basis of  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopic assay (singlet,  $\delta +52.18$ ); upon allowing the reaction mixture to stand at 253 K 2,2,6,6-tetramethylpiperidinium bromide crystallized. Crystal  $0.3 \times 0.3 \times 0.2$  mm, mounted in Lindemann-glass tube,  $\theta_{\text{max}} = 23^\circ$  ( $h_{\text{max}} = 9$ ,  $k_{\text{max}} = 10$ ,  $l_{\text{max}} = 14$ ), Nonius CAD-4 diffractometer, Mo  $K\alpha$ , graphite monochromated; 994 unique reflections measured, 883 classed as observed with  $I > 2\sigma(I)$ , no absorption correction, no crystal decay apparent from monitoring two standard reflections; structure solved with direct methods (*MULTAN77*: Main, Lessinger, Woolfson, Germain & Declercq, 1977), isotropic refinement of all non-hydrogen atoms,  $R = 0.12$  (*SHELX*: Sheldrick, 1976), all hydrogen atoms visible in difference Fourier maps, methyl hydrogen atoms refined as rigid groups ( $\text{C}-\text{H} = 1.08 \text{ \AA}$ ,  $\text{H}-\text{C}-\text{H} = 109.4^\circ$ ) and, for each methyl group, hydrogen atoms constrained to have same isotropic temperature factor; positional and isotropic thermal parameters for remaining hydrogen atoms refined without constraints; in final cycles of full-matrix least-squares refinement based on  $F$ , all non-hydrogen atoms refined anisotropically, 148 parameters,  $A_{\text{max}}/\sigma = 0.03$ , max.  $\Delta\rho$  excursions on final difference map  $< 0.5 \text{ e \AA}^{-3}$  (all near  $\text{Br}^-$  ion); weighting scheme which gave best analysis of variance in ranges of  $|F|$  and in  $\theta$  was  $w = 1/[\sigma^2(F) + 0.005 F^2]$ ,  $R = 0.040$ ,  $R_w = 0.052$ ; \* atomic scattering factors of *SHELX* used.

**Discussion.** Fractional coordinates are given in Table 1. Bond lengths, angles and selected torsion angles are given in Table 2. The molecule with its atomic numbering is shown in Fig. 1.

The piperidinium ion adopts a distorted chair conformation with almost exact mirror symmetry. Chemically equivalent bond lengths are all equal to within one standard deviation. The axial  $\text{C}(2)-\text{C}(8)$  and  $\text{C}(6)-\text{C}(7)$  bonds are longer by  $0.02 \text{ \AA}$  than the  $\text{C}-\text{C}_{\text{eq}}$  bonds; an effect which may be a consequence of the  $\text{C}_{\text{ax}} \cdots \text{C}_{\text{ax}}$  steric interaction. The narrow  $\text{N}-\text{C}-\text{C}_{\text{eq}}$  bond angles of  $105^\circ$  have also been found in two other comparable 2,2,6,6-tetramethylpiperidine compounds: 4-ethynyl-2,2,6,6-tetramethyl-4-piperidinol (I) (Cygler, Grabowski, Skolimowski & Skowroński, 1978) and

*N,N'*-bis(2,2,6,6-tetramethyl-4-piperidyl)succinamide (II) (Ruben, Zalkin & Templeton, 1974). The  $\text{C}-\text{N}$  bond lengths of  $1.525$  and  $1.532 \text{ \AA}$  are on average  $0.03 \text{ \AA}$  longer than comparable bonds in all neutral substituted 2,2,6,6-tetramethylpiperidine compounds in the literature: (I), (II), 1,2,2,6,6-pentamethyl-4-vinyl-4-piperidinol (III) (Cygler, Dobrynin & Perrin, 1980), 1,2,2,4,6,6-hexamethyl-4-piperidinol (IV) (Cygler, Skarżyński & Skolimowski, 1980), 4-*tert*-butyl-4-hydroxy-1,2,2,6,6-pentamethylpiperidine (V) (Cygler, Markowicz, Skolimowski & Skowroński, 1980). The only charged 2,2,6,6-tetramethylpiperidine compound in the literature [2,2,6,6-tetramethyl-4-piperidinone-HCl (VI) (Rees & Weiss, 1971)] has long  $\text{C}-\text{N}$  bonds of  $1.521 \text{ \AA}$ . It appears, therefore, that the nitrogen lone-pair electrons of the neutral compounds are incorporated to some extent into the  $\text{C}-\text{N}$  bonds.

Though the nitrogen atom may be regarded as  $sp^3$  hybridized, the CNC angle is  $120.9 (5)^\circ$ . This compares with values found in compounds (I) through (VI) which lie in the range  $116$  to  $120^\circ$ . This general widening of the CNC angle and resulting distortion of the ring chair conformation may be explained by non-bonded van der Waals repulsion between axial methyl groups. Most unsubstituted piperidine molecules (e.g. Alcock, Hagger, Harrison & Wallbridge, 1982) or

Table 1. Fractional coordinates of atoms with e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^*(\text{\AA}^2)$
Br(1)	0.18983 (8)	0.17554 (7)	0.28661 (5)	0.0435
N(1)	0.3319 (6)	0.1751 (6)	0.7335 (4)	0.0275
C(2)	0.2648 (9)	0.2635 (8)	0.8205 (5)	0.0356
C(3)	0.2648 (10)	0.4221 (8)	0.7852 (7)	0.0452
C(4)	0.1913 (12)	0.4421 (8)	0.6807 (7)	0.0530
C(5)	0.2728 (8)	0.3544 (8)	0.6002 (6)	0.0430
C(6)	0.2746 (8)	0.1921 (7)	0.6237 (5)	0.0337
C(7)	0.1186 (8)	0.1232 (9)	0.6125 (6)	0.0448
C(8)	0.1068 (9)	0.2098 (10)	0.8494 (6)	0.0523
C(9)	0.3870 (10)	0.1120 (10)	0.5576 (5)	0.0503
C(10)	0.3704 (10)	0.2407 (10)	0.9096 (5)	0.0541

\* $U_{\text{eq}} = \frac{1}{3} \text{ trace } U$ .

Table 2. Bond lengths ( $\text{\AA}$ ), angles ( $^\circ$ ) and selected torsion angles ( $^\circ$ )

N(1)-C(2)	1.525 (9)	N(1)-C(6)	1.532 (8)
C(2)-C(3)	1.546 (11)	C(5)-C(6)	1.541 (10)
C(3)-C(4)	1.528 (12)	C(4)-C(5)	1.516 (12)
C(2)-C(8)	1.538 (10)	C(6)-C(7)	1.534 (11)
C(2)-C(10)	1.512 (11)	C(6)-C(9)	1.517 (11)
C(6)-N(1)-C(2)	120.9 (5)	C(5)-C(4)-C(3)	110.6 (7)
N(1)-C(2)-C(3)	107.0 (6)	N(1)-C(6)-C(5)	107.0 (5)
N(1)-C(2)-C(8)	111.5 (6)	N(1)-C(6)-C(7)	110.3 (5)
N(1)-C(2)-C(10)	105.0 (6)	N(1)-C(6)-C(9)	105.4 (5)
C(3)-C(2)-C(8)	112.5 (6)	C(5)-C(6)-C(7)	112.4 (6)
C(3)-C(2)-C(10)	111.3 (6)	C(5)-C(6)-C(9)	111.9 (6)
C(8)-C(2)-C(10)	109.3 (6)	C(7)-C(6)-C(9)	109.6 (6)
C(2)-C(3)-C(4)	112.5 (7)	C(6)-C(5)-C(4)	113.1 (6)
C(6)-N(1)-C(2)-C(3)	-50.0 (8)	C(2)-N(1)-C(6)-C(5)	49.5 (7)
N(1)-C(2)-C(3)-C(4)	51.7 (8)	N(1)-C(6)-C(5)-C(4)	-51.2 (8)
C(2)-C(3)-C(4)-C(5)	-59.3 (9)	C(6)-C(5)-C(4)-C(3)	59.2 (9)
H(4)-C(8)-C(2)-C(3)	48.2 (11)	H(1)-C(7)-C(6)-C(5)	-51.0 (10)
H(10)-C(10)-C(2)-C(3)	64.3 (9)	H(7)-C(9)-C(6)-C(5)	-52.5 (9)

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38829 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

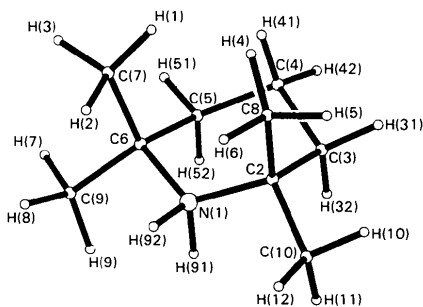


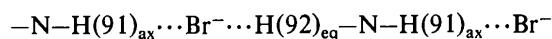
Fig. 1. View of the molecule showing the atom numbering.

piperazinium molecules (*e.g.* Vanier & Brisse, 1982) have much narrower CNC angles in the range 110 to 114°.

The  $C(7)_{ax} \cdots C(8)_{ax}$  distance of 3.205 (11) Å is the shortest yet observed in 2,2,6,6-tetramethylpiperidine molecules and is consistent with a trend showing increasing  $C_{ax} \cdots C_{ax}$  distance with increasing bulk of the 4-substituent; *e.g.* (I) (ethynyl) 3.214 (5) Å; (III) (vinyl) 3.264 (6) Å; (IV) (methyl) 3.271 (7) Å; (V) (*tert*-butyl) 3.383 (5) Å. Non-bonded H $\cdots$ H contacts between the axial methyl groups are particularly short with  $H(1) \cdots H(4) = 1.99$  Å and  $H(2) \cdots H(8) = 2.34$  Å. Such interactions cause a significant flattening of the ring at nitrogen but leave the two C—C—C—C dihedral angles near the fully puckered values of  $\pm 60^\circ$  (Table 2).

The near perfect mirror symmetry of the cation is broken only by the different conformations of the two equatorial methyl groups caused by interactions between the bromide ion and the methyl hydrogen on

C(7). Molecular packing is dominated by the hydrogen-bonded chains



with  $Br \cdots H_{ax} = 2.52$  (6) and  $Br \cdots H_{eq} = 2.49$  (6) Å.

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## The Structure of *N*-[3-(3-Ammoniopropylammonio)propyl]succinamic Acid Sulfate, $C_{10}H_{23}N_3O_3^{2+} \cdot SO_4^{2-}$

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**Abstract.**  $M_r = 329.37$ ,  $P2_1/c$ ,  $a = 17.693$  (2),  $b = 9.453$  (1),  $c = 8.958$  (1) Å,  $\beta = 90.42$  (2)°,  $V = 1498.2$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 704$ ,  $D_m = 1.460$ ,  $D_x = 1.457$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu(\text{Cu } K\alpha) = 22.25$  cm<sup>-1</sup>,  $T = 298$  K,  $R = 0.042$  for

2278 reflections. The backbone chain in the cation consists of four short segments which are in the extended conformation. The N-terminus segment is six atoms in length and it is followed by two five-atom segments [N(2)C(7)C(6)C(5)N(1) and C(5)N(1)C(4)C(3)C(2)] and one four-atom segment [C(3)C(2)C(1)O(1)]. The chain changes direction abruptly at the three junctions between segments. The

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